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Engberg, Sara Lena Josefin; Crovetto, Andrea; Bosco, Edoardo; Rasmussen, Philip; Hansen, Ole; Schou, Jørgen

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# Annealing in Sulfur of Doctor Bladed CZTS Nanoparticles

Sara Engberg<sup>(1)</sup>, Andrea Crovetto<sup>(2)</sup>, Edoardo Bosco<sup>(2)</sup>, Philip Rasmussen<sup>(2)</sup>, Ole Hansen<sup>(2)</sup>, Jørgen Schou<sup>(1)</sup>

<sup>(1)</sup>DTU Fotonik, Technical University of Denmark

<sup>(2)</sup>DTU Nanotech, Technical University of Denmark

In this work, we investigate the influence of sulfur content on grain growth during annealing in 10 mbar nitrogen atmosphere.

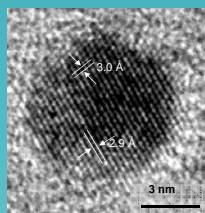
## Motivation

Solar cells made from nanoparticles of copper zinc tin sulfide (CZTS) from solution-processing are expected to be comparatively inexpensive. However, (1) the high carbon content in nanoparticle thin films is one of the main limitations for this approach, and (2) grain boundaries and defects are believed to be a site for recombination that limits the efficiency. Annealing in vacuum and/or a nitrogen atmosphere facilitates grain growth and improves the electronic properties. Annealing in selenium shows the best results, however annealing in sulfur has the advantage of leading to a non-toxic material.

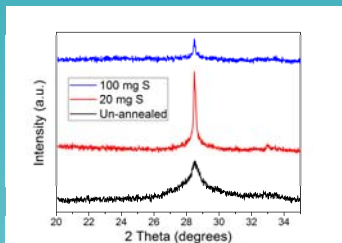
## Nanoparticle synthesis

Nanoparticles were synthesized through hot-injection with oleylamine as the solvent.

The average particle size was  $8.3 \pm 4.0$  nm, and composition  $\text{Cu}_{1.7}\text{Zn}_{1.5}\text{Sn}_{0.86}\text{S}_4$ .



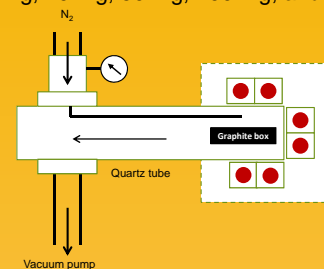
HRTEM image of CZTS nanoparticle from ink.



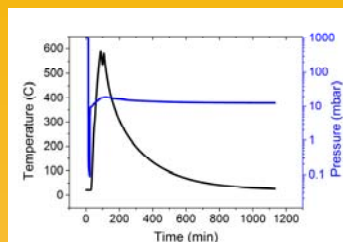
XRD pattern of CZTS before and after annealing.

## Annealing

Annealing is carried out in a graphite box in a quartz tube, with a heating ramp of  $11.7^\circ\text{C}/\text{min}$  and natural cooling (i.e. 10 hours in our setup). We investigated annealing with the following amounts of S: 0 mg, 20 mg, 50 mg, 100 mg, and 200 mg.



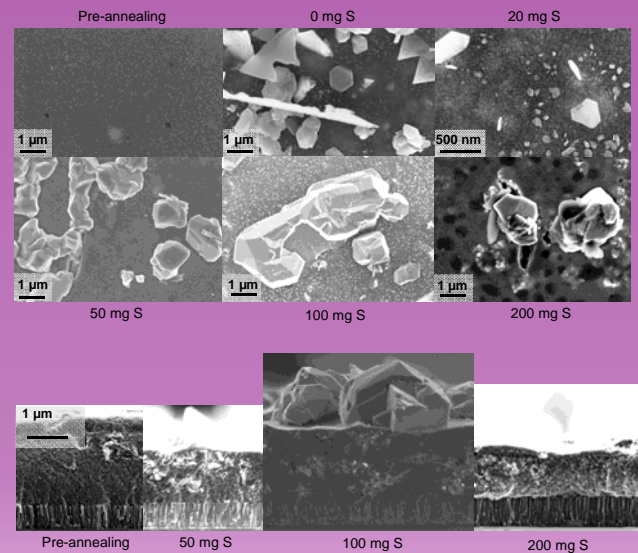
Schematic drawing of tube furnace.



Temperature and pressure profile during annealing.

## Results: Grain growth

SEM images show large grains grown on top of the surface for all sulfur contents. For 0 mg S we see plate-like grains, and when more S is added the grains become columnar. The largest grains were seen for 100 mg S. No distinctive difference was seen for the cross-sections.



## Results: Elemental losses

S-content in film before annealing: 48%

Average S-content in film after annealing: 54%

The sulfur content in the film was found not to vary with amount of sulfur in the graphite box. Neither did we see a difference in sulfur content in the film when doing EDX through the cross-section of the film.

## Composition of large grains:

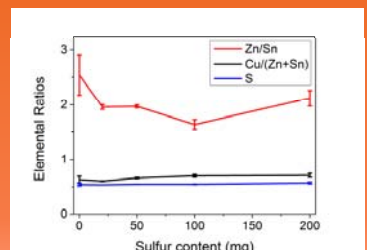
$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.82$

$\text{Zn}/\text{Sn} = 1.32$

## Average composition of film:

$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.65$

$\text{Zn}/\text{Sn} = 2.0$



## Conclusion

We find that adding sulfur in the range between 0 mg and 200 mg for annealing does not affect the composition when annealing nanocrystal thin films in a graphite box. Grains were formed mainly on top of the film surface, and the largest ones were observed at 100 mg S content.

## Acknowledgement

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